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MINED FROM THE MIOCENE AURIFEROUS
GRAVELS OF CALIFORNIA

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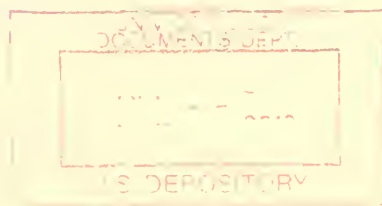
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COMPOSITION OF THREE FOSSIL WOODS MINED FROM THE

MIOCENE AURIFEROUS GRAVELS OF CALIFORNIA¹

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The Forest Products Laboratory has recently analyzed three old woods which were mined from the Miocene auriferous gravels of California and submitted to the Laboratory by Prof. I. W. Bailey of Bussey Institute of Boston, Mass. The woods are a pine of the hard-pine class of which ponderosa pine is a member, a cedrus, which family is extinct in the Western Hemisphere, and a sequoia of the family of which redwood is a member. These woods were mined about 200 feet below the surface of the ground. For the want of a better name these old residual materials are referred to here as fossil woods.

These fossil woods had developed a pronounced brown discoloration, extreme brashness, and in some small areas of the structure, mineral-like properties characteristic of petrified woods. An examination with the aid of a microscope revealed no signs of fungous attack. Many of the structural elements were observed to be twisted and crushed perhaps as the result of excessive pressures during their burial underground. Fibers which had undergone no deformation still manifested a preferred orientation of their cellulosic structure when observed between nicol prisms with corresponding axes arranged at 90° to one another.

Analytical Procedures Employed

The fossil materials were reduced to sawdust which passed through a 40-mesh sieve but was retained on a 60-mesh sieve. The materials were analyzed for extractives, pentosans, methoxyl, lignin, and cellulose by the standard methods employed at the Forest Products Laboratory.²

¹Presented before the American Chemical Society at St. Petersburg, Fla., March 1934.

²(a) Bray, Paper Trade Jour., 87, 59-68 (1928); (b) Ritter, Seborg & Mitchell, Ind. Eng. Chem., Anal. Ed., 4, 202 (1932); (c) Ritter & Ilick, Ind. Eng. Chem., 16, 147 (1924).

In the determination of cellulose in the fossil woods it was necessary to prolong the chlorination periods beyond 5 minutes, the time used for normal woods,^{2c} because the fossil wood lignin was less reactive to chlorine than that from normal wood. Another difficulty experienced in determining the cellulose in the fossil woods was the tendency of the partially delignified cellulose to gelatinize, causing difficulties in filtering and washing. This tendency toward gelatinization was overcome by adding a few cubic centimeters of dilute hydrochloric acid. In the final washing the hydrochloric acid was removed by means of water and alcohol.

Results of the analyses are recorded in the accompanying table. For comparison the table also includes analytical data on the composition of two normal woods of similar species.

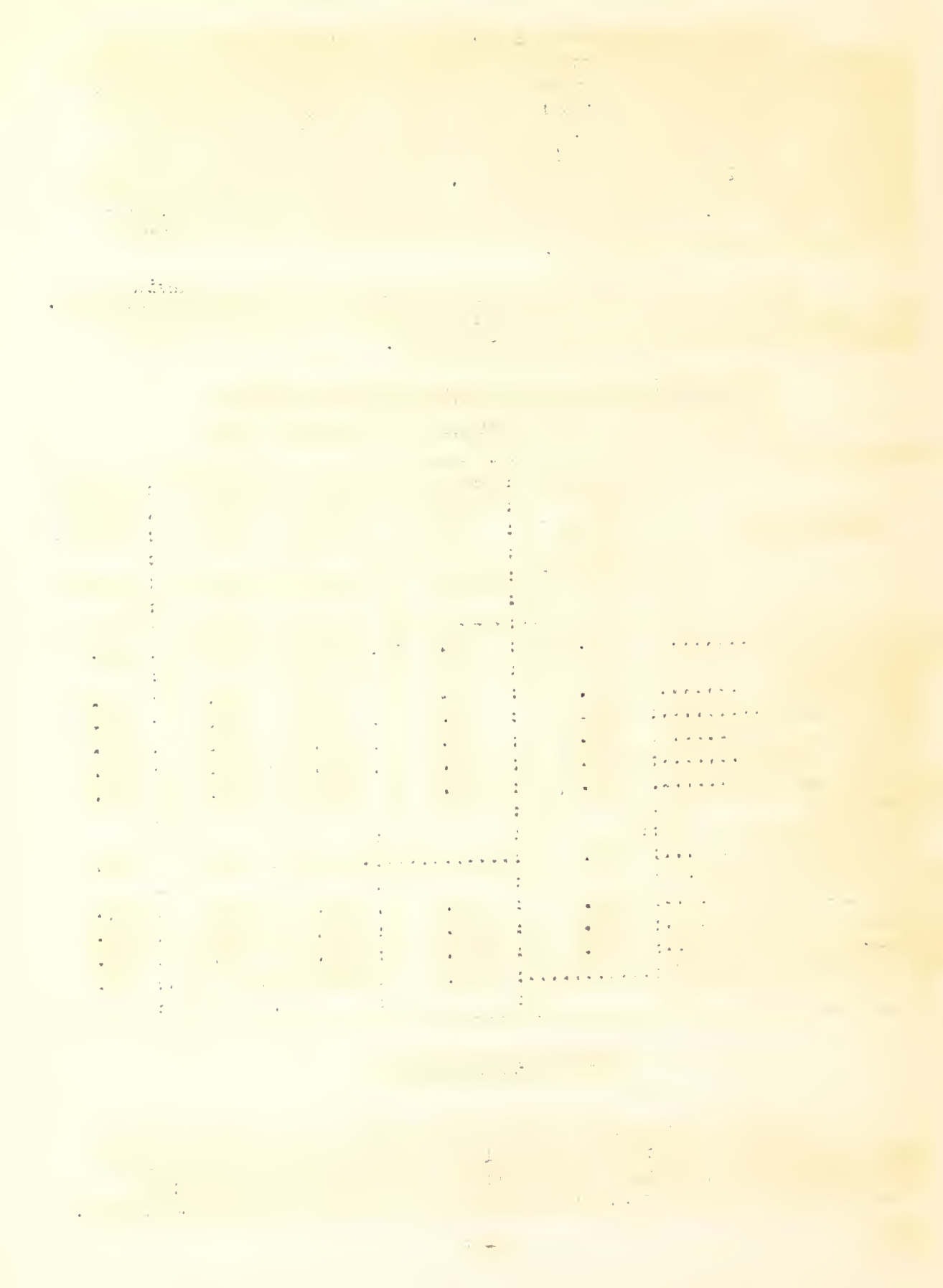
Composition of Three Fossil and Two Normal Woods

Results based on the weight of the oven-dry woods

Determination	: Ponderosa : pine : (normal : wood), : percent	: Hard pine : (fossil : wood), : percent	: Cedrus : (fossil : wood), : percent	: Redwood : (normal : wood), : percent	: Sequoia : (fossil : wood), : percent
1	2	3	4	5	6
Ash.....	0.46	3.80	1.50	0.21	2.50
Solubility in:					
Cold water.....	4.09	.63	.40	7.36	.87
Hot water.....	5.05	.88	.42	9.86	1.54
Ether.....	8.52	.54	.27	1.07	.24
1 percent NaOH.....	20.30	4.66	3.07	20.00	11.10
Pentosan.....	8.97	4.58	3.87	10.55	4.56
Pentosan in:					
Cross and Bevan	:	:	:	:	:
cellulose.....	5.05	4.06	1.96
Cross and Bevan cell-	:	:	:	:	:
ulose.....	57.41	5.00	13.10	48.45	51.60
Lignin.....	26.65	90.20	84.70	34.20	45.60
CH ₃ O.....	4.49	12.50	11.20	5.21	5.60
CH ₃ O recovered in lignin.....	:	12.60	11.40	5.65
	:	:	:	:	:

Discussion of Results

A general comparison of the composition of the fossil and the normal woods shows that the fossil pine is markedly lower in water and ether extractives, pentosans and cellulose than the normal pine; the fossil sequoia is lower in water and ether extractives and pentosans than



the normal sequoia. These losses are in general agreement with Komatsu,³ who found that fossil woods had lost a portion of their extractives and carbohydrates. In both the fossil pine and sequoia the alkali-soluble content was markedly lower than that of the corresponding normal woods, which indicates absence of decay. On the other hand, the fossil pine is much higher in ash and lignin than the normal pine; the fossil sequoia is higher not only in ash and lignin but also in cellulose than its normal species.

When a complex material undergoes a selective decomposition that removes certain constituents in greater proportion than others, a comparison of the percentage composition of the decomposed material with that of the original does not afford a direct or accurate means of determining the relative losses of the different constituents. It is readily possible, however, to obtain a satisfactory basis for direct comparison by determining the minimum weight loss required to give the percentage composition found for the decomposed material and then recalculating to the basis of percentage of the original material. The minimum weight loss required is such that one constituent shows no change. This constituent will be the one that shows the greatest percentage increase in the residue.

Hard Pine.---Excluding ash, which is known to increase in weight upon petrification, the constituent in the fossil pine that shows the greatest percentage increase is lignin. Whether the lignin has suffered losses due to hydrolysis⁴ and decay⁵ is not known. If it is assumed that no loss has occurred in the fossil-pine lignin the residue would be approximately 29.5 percent ($26.65/90.20 \times 100 = 29.5$) of the original wood. In other words, the fossil pine has lost 70.5 percent of its original weight.

The lignin of the fossil pine has a methoxyl content of 14.0 percent, which is in fairly close agreement with that of lignin from normal ponderosa.⁶ All of the methoxyl in the fossil pine is recovered in the isolated lignin, indicating that any methoxyl associated with the carbohydrates has been removed during the partial disintegration of the wood.

The ash content of the fossil pine is high when calculated on the basis of the original wood, being 1.12 percent. This is likely due to some small areas which are indicative of petrification.

³Komatsu and Ueda, Mem. Coll. Sci. Kyoto Imp. Univ. 7A, 7-13 (1923).

⁴Hawley and Campbell, Ind. Eng. Chem., 19, 742 (1927).

⁵Bray, Paper Trade Jour., 78, 58 (1924).

⁶Ritter, Ind. Eng. Chem., 15, 1265 (1923).

Cedrus.--No normal cedrus was available for analysis. However, a comparison of the composition of other softwoods with that of the fossil cedrus reveals that the latter has undergone changes similar to those of the fossil pine.

Sequoia.--As with the pine, if ash is excluded and it is assumed that no loss has occurred in the lignin of the fossil sequoia, the weight of the residue would be 75.0 percent of that of the original wood, showing a loss of 25 percent. On this basis the recalculated value of the fossil cellulose would be only 38.7 percent of the normal wood, showing an apparent loss of 9.7 percent.

Lignin from the fossil sequoia has a methoxyl content of 12.6 percent as compared with 16.2 percent found in lignin from normal redwood.¹ This finding indicates that some of the methoxyl groups have been removed from the lignin of the fossil sequoia.

A comparison of the methoxyl in the wood and in the lignin indicates that all of the methoxyls found in the fossil wood are associated with lignin.

The ash content in the sequoia is unusually high on the basis of normal wood, being 1.87 percent. In the sequoia also were localized areas which indicated the beginning of petrification which would account for high ash content.

Microstructure of the Cross and Bevan Cellulose.--Microscopical examinations of the Cross and Bevan cellulose residues from the fossil woods disclosed that the cellulose residue of the fibers had been reduced to thin-walled structures. A high percentage of these structures were collapsed, their fibrils loosened from one another, indicating that materials between the fibrils had been removed. The residue is free of hyphae, which suggests that the loss in wood constituents is due to hydrolysis rather than fungous attack. Loss of weight through hydrolysis rather than decay is also suggested by the low alkali-soluble content of the fossil materials.

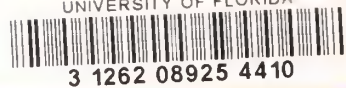
Acknowledgments.--The authors further acknowledge receiving the woods through the kindness of I. W. Bailey of the Bussey Institute, R. W. Chaney of the University of California, and E. F. Smith of the Eldorado National Forest; identification of the specimens by G. J. Griffin of the Forest Products Laboratory and by I. W. Bailey; examination for indications of decay by C. A. Richards of the Bureau of Plant Industry.

¹Dorl, Ind. Eng. Chem., 12, 478 (1920).

Summary

Samples of pine, cedrus, and sequoia woods mined from the Miocene auriferous gravels about 200 feet below the surface of the ground in California have been analyzed. A marked decrease has occurred in the extraneous and the carbohydrate content of the woods. On the other hand, the lignin content of the residues is abnormally high as compared with that of a normal wood of the same genus. On the basis of the original wood, the lignin has decreased less than any other constituent.

Microscopical examinations of the residue and the relation between the alkali solubility and cellulose content of the fossil woods indicate that decomposition was due to agencies other than fungous attack. Hydrolysis appears likely.



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